

~~DESCRIPTION~~

METHOD FOR FORMING SILICON FILM AND INK COMPOSITION FOR INK

JET

BACKGROUND OF THE INVENTION

~~TECHNICAL FIELD~~

Field of the Invention

The present invention relates to an ink composition containing a silicon

precursor for forming, by patterning, a silicon film by an ink jet process in use of LSIs, thin film transistors, and photosensitive devices, and to a method for forming a silicon film by an ink jet process.

10 Description of the Related Art

BACKGROUND ART

As conventional methods for forming amorphous silicon films and polysilicon films, thermal CVD (chemical vapor deposition) processes, plasma enhanced CVD processes, and photo-assisted CVD processes using monosilane gas and disilane gas have been used. In general, thermal CVD processes are widely used for polysilicon films (refer to J. Vac. Sci. Technology, Vol. 14, 1082 (1977)), and plasma enhanced CVD processes are widely used for amorphous silicon films (refer to Solid State Com., Vol. 17, 1193 (1975)). These are used in production of liquid crystal devices having thin film transistors and solar batteries.

20 In the formation of silicon films by these CVD processes, however, further
improvements are needed with regard to the following problems: (1) The production
yield is low due to system contamination and the formation of foreign materials,
which are caused by silicon particles generated during the gas phase reaction; (2) A
uniform film thickness is barely obtainable on a substrate having an uneven surface
25 due to gaseous raw materials; (3) The productivity is low due to a low deposition rate
of the film; and (4) The plasma enhanced CVD process requires a complicated and
expensive radiofrequency generator and vacuum equipment.

In regard to materials used in the CVD process, the use of silicon hydride, which is highly reactive gas, is difficult to handle, and requires hermetic vacuum

equipment. This apparatus is both complicated to operate and expensive. Moreover, both the vacuum system and the plasma system consume a large amount of energy, resulting in high production costs.

5 In recent years, a method has been proposed for applying liquid silicon hydride without a vacuum system. Japanese Unexamined Patent Application Publication No. 1-29661 discloses a method for forming a silicon-based thin film in which a gaseous material is liquefied and is adsorbed onto a cooled substrate to react with chemically active, atomic hydrogen. This method, however, has the following problems. Since silicon hydride is required as the raw material for the process, and is 10 continuously gasified and cooled, a complicated apparatus is required and the control of the thickness is difficult.

An example of solid silicon hydride polymers is reported in Great Britain Patent No. GB-2,077,710A. Since this polymer is insoluble in solvents, the film is not formed by coating.

15 Moreover, Japanese Unexamined Patent Application Publication No. 9-237927 discloses a method for spray-coating a polysilane solution onto a substrate having a large area and for pyrolyzing the coating to form a silicon film, in order to produce solar batteries. In carbon-containing silicon compounds, a large amount of carbon remains as an impurity in pyrolysis or photolysis by ultraviolet irradiation, 20 hence, it is difficult to prepare an amorphous or polycrystalline silicon film having superior electrical characteristics.

The silicon semiconductor film is generally doped with a Group III element or a Group V element in the Periodic Table and is used as a p-type or n-type semiconductor. After the formation of the silicon film, doping using these elements is 25 generally performed by thermal diffusion and ion implantation. Since the doping is performed *in vacuo*, process control is complicated, and it is particularly difficult to form a uniformly doped silicon film onto a large substrate.

On the other hand, the above Japanese Unexamined Patent Application Publication No. 9-237927 discloses a method for applying a polysilane solution

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containing an alkyl compound which imparts p-type or n-type conductivity and a method for pyrolyzing a coating film from a polysilane solution in an atmosphere containing a dopant source. In the former method, however, a uniformly doped film may be unobtainable due to differences in solubility between the polysilane and the 5 dopant-containing alkyl compound, and the final film product inevitably contains a large amount of carbon as an impurity due to carbon contained in the material, as described above. In the latter method, it is difficult to control the dopant.

In a conventional method for forming a silicon film pattern, a silicon film is formed on the entire substrate by the above method, and a required pattern is formed 10 by a photolithographic process or an etching process. When the silicon film is patterned over a large area to form many devices, many production steps must be employed and expensive apparatus and various materials are used, requiring a large amount of energy, which results in high production costs.

Summary of the Invention

DISCLOSURE OF INVENTION

It is an object of the present invention to provide a composition, which is a material for stably forming a desired silicon film pattern with low energy consumption at low cost, and a method for forming a silicon film without a conventional vacuum process, photolithography, and etching, in the production of a 20 device having a desired silicon film pattern onto a substrate having a large area. It is another object to provide a composition containing a silicon precursor and a method for patterning a silicon film, in the production of a device having a silicon film doped with boron or phosphorus in which a film comprising a modified silicon compound as a silicon precursor is formed using a solution, and the silicon precursor film is converted into semiconductive silicon and doping is simultaneously achieved by heat 25 and/or light treatment in an inert atmosphere.

According to the present invention, there is provided a method for forming a silicon film, comprising; applying by patterning an ink composition containing a silicon compound onto a substrate by an ink jet process.

Moreover, the present inventors have intensively researched to achieve the above objects and have discovered that an ink material composition containing a silicon compound represented by the following general formula (I) or (II) exhibits superior material stability, discharge stability, and coating uniformity in an ink jet process, and that the required silicon film pattern can be formed on a substrate by heat and/or light treatment of a silicon precursor coating film from the solution, with satisfactory conversion into the silicon film without incorporation of a solvent.

According to the present invention, there is provided a method for a silicon film pattern, comprising: applying by patterning a composition containing a silicon compound represented by the following general formula (I) or (II) onto a substrate by an ink jet process:



with n representing an integer 3 or more, m representing an integer of n, 2n-2, 2n, or 2n+2, and X representing a hydrogen atom and/or a halogen atom; and



with X representing a hydrogen atom and/or a halogen atom, Y representing a boron atom or a phosphorus atom, a representing an integer of 3 or more, b representing an integer of a to 2a+c+2, and c representing an integer of 1 to a.

It is preferable to use a mixture of the silicon compound represented by the general formula (I) and the silicon compound represented by the general formula (II).

According to the present invention, there is provided a liquid composition containing a silicon compound for ink jet processes comprising a silicon compound represented by the general formula (I) and/or a silicon compound represented by the general formula (II), and a solvent for dissolving the silicon compound, the solvent having a specific viscosity, a specific surface tension, and a specific solid component content.

DO NOT DESTROY

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a drawing showing patterning steps of a silicon thin film by an ink jet process in accordance with Example 1.

5 Fig. 2 is a drawing showing patterning steps of a silicon thin film by an ink jet process in accordance with Example 2.

Fig. 3 is a drawing showing patterning steps of a p-type silicon thin film by an ink jet process in accordance with Example 3.

Fig. 4 is a drawing showing patterning steps of an n-type silicon thin film by an ink jet process in accordance with Example 4.

10 Fig. 5 is a drawing showing patterning steps of a silicon thin film by an ink jet process in accordance with Example 5.

Fig. 6 is a drawing showing patterning steps of a p-type silicon thin film by an ink jet process in accordance with Example 6.

15 Fig. 7 is a drawing showing patterning steps of a silicon thin film by an ink jet process in accordance with Example 7.

fl Detailed Description of the Embodiments
BEST MODE FOR CARRYING OUT THE INVENTION

The embodiments of the present invention will be described in detail.

20 The silicon compounds used in the method for forming the silicon film in the present invention are preferably compounds represented by the general formula (I) Si_nX_m with n representing an integer 3 or more, m representing an integer of n, $2n-2$, $2n$, or $2n+2$, and X representing a hydrogen atom and/or a halogen atom, and compounds represented by the general formula (II) $Si_aX_bY_c$ with X representing a hydrogen atom and/or a halogen atom, Y representing a boron atom or a phosphorus atom, a representing an integer of 3 or more, b representing an integer of a to $2a+c+2$, and c representing an integer of 1 to a.

25 In these general formulae (I) and (II), n represents an integer of 3 or more, and a+c represents an integer of 4 or more. In consideration of thermodynamic stability, solubility, and feasibility of purification, cyclic silicon compounds with n of

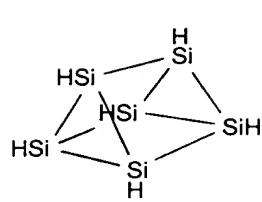
approximately 5 to 20 and particularly 5 or 6 are preferred in the general formula (I), and silicon compounds with $a+c$ of approximately 5 to 20 and particularly 5 or 6 are preferred in the general formula (II). At a value of less than 5, the silicon compound is unstable due to distortion of the ring and handling is difficult. When n and $a+c$ are larger than 20, the solubility decreases due to cohesive force of the silicon compound and selectable solvents are limited.

In the general formulae (I) and (II) for the silicon compounds used in the present invention, X represents a hydrogen atom and/or a halogen atom. Since these silicon compounds are precursors for the silicon films, the silicon compounds must be finally converted into amorphous or polycrystalline silicon by heat and/or light treatment. During the final conversion process, the silicon-hydrogen bonds and the silicon-halogen bonds are cleaved to form silicon-silicon bonds, and converted into silicon. Examples of halogen atoms, include: a fluorine atom, a chlorine atom, a bromine atom, and an iodine atom. Chlorine and bromine are preferable with regard to the bond cleavage. X may be a hydrogen atom alone or a halogen atom alone, or may be a partially halogenated compound, in which the sum of hydrogen atoms and halogen atoms satisfies the general formula (I) or (II).

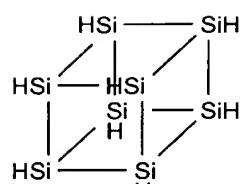
Examples of the silicon compounds represented by the general formula Si_nX_m used in the present invention will be described. Examples of the compounds of $m = 2n+2$ include silane hydrides, such as: trisilane, tetrasilane, pentasilane, hexasilane, and heptasilane, and substituted compounds thereof in which hydrogen atoms are partially or completely replaced with halogen atoms. Examples of $m = 2n$ compounds include: monocyclic silicon hydride compounds, such as: cyclotrisilane, cyclotetrasilane, cyclopentasilane, silylcyclopentasilane, cyclohexasilane, silylcyclohexasilane, and cycloheptasilane; and halogenated cyclic silicon compounds thereof in which hydrogen atoms are partially or completely replaced with halogen atoms, such as hexachlorocyclotrisilane, trichlorocyclotrisilane, octachlorocyclotetrasilane, tetrachlorocyclotetrasilane, decachlorocyclopentasilane, pentachlorocyclopentasilane, dodecachlorocyclohexasilane,

hexachlorocyclohexasilane, tetradecachlorocycloheptasilane,
heptachlorocycloheptasilane, hexabromocyclotrisilane, tribromocyclotrisilane,
pentabromocyclotrisilane, tetrabromocyclotrisilane, octabromocyclotetrasilane,
tetrabromocyclotetrasilane, decabromocyclopentasilane, pentabromocyclopentasilane,
5 dodecabromocyclohexasilane, hexabromocyclohexasilane,
tetradecabromocycloheptasilane, and heptabromocycloheptasilane. Examples of
compounds of $m = 2n-2$ include dicyclic silicon hydride compounds, such as 1,1'-
biscyclobutasilane, 1,1'-biscyclopentasilane, 1,1'-biscyclohexasilane, 1,1'-
biscycloheptasilane, 1,1'-cyclobutasilylcyclopentasilane, 1,1'-
10 cyclobutasilylcyclohexasilane, 1,1'-cyclopentasilylcycloheptasilane, 1,1'-
cyclopentasilylcyclohexasilane, 1,1'-cyclopentasilylcycloheptasilane, 1,1'-
cyclohexasilylcycloheptasilane, spiro[2,2]pentasilane, spiro[3,3]heptasilane,
spiro[4,4]nonasilane, spiro[4,5]decasilane, spiro[4,6]undecasilane,
spiro[5,5]undecasilane, spiro[5,6]dodecasilane, and spiro[6,6]tridecasilane;
15 substituted silicon compounds in which hydrogen atoms are partly or completely
replaced with SiH_3 groups or halogen atoms. Moreover, examples of compounds of
 $m = n$ include polycyclic silicon hydride compounds, such as Compounds 1 to 5
represented by the following formulae, and substituted silicon compounds thereof in
which hydrogen atoms are partially or completely replaced with SiH_3 groups or
20 halogen atoms. These compounds may be used as a mixture of two or more types.

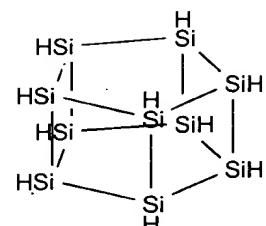
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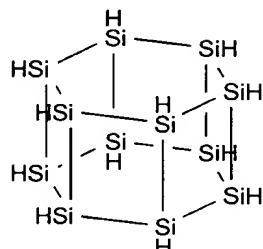
Compound 1



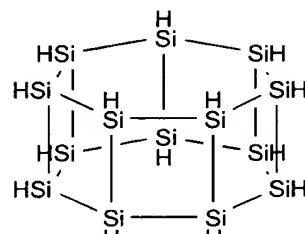
Compound 2



Compound 3



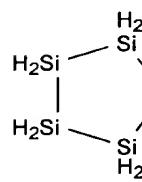
Compound 4



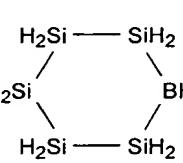
Compound 5

Examples of the compounds represented by the general formula (II) $Si_aX_bY_c$

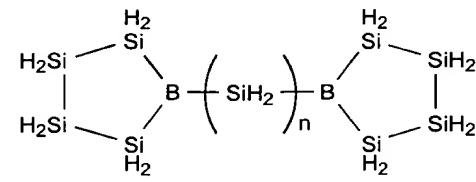
5 used in the present invention include modified silane compounds as shown in Compounds 6 to 27 represented by the following formulae.



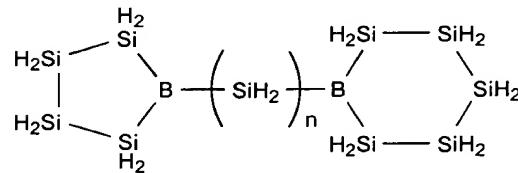
Compound 6



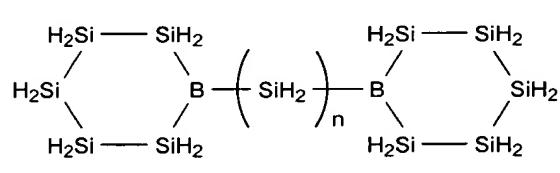
Compound 7



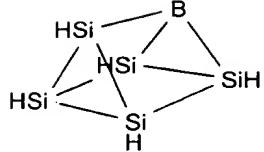
Compound 8



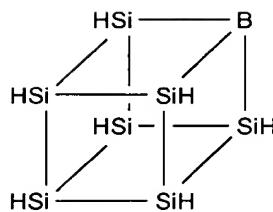
Compound 9



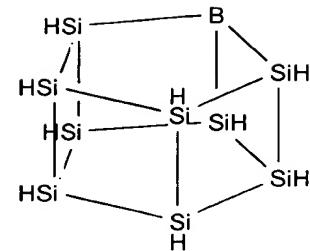
Compound 10



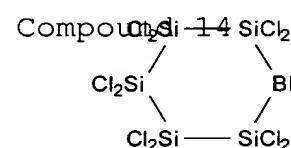
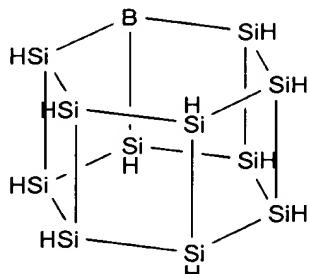
Compound 11



Compound 12

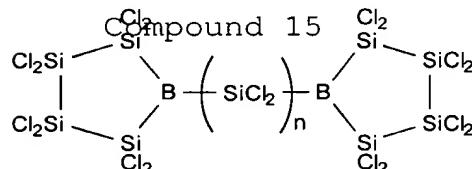
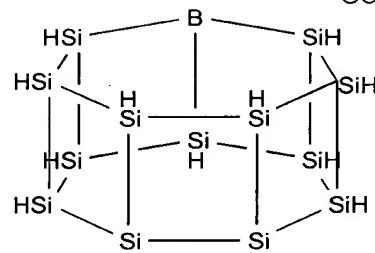


Compound 13

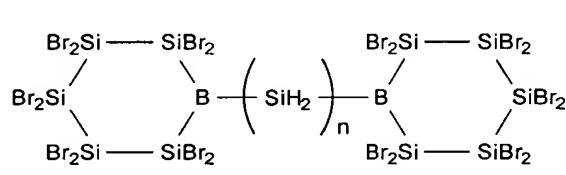
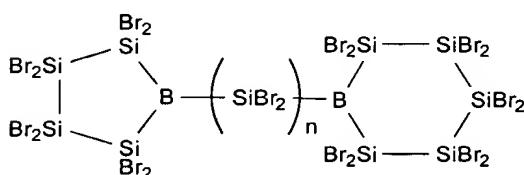


Compound 16

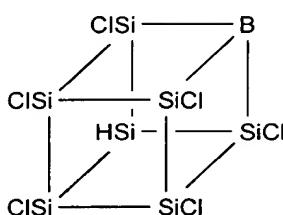
Compound 17



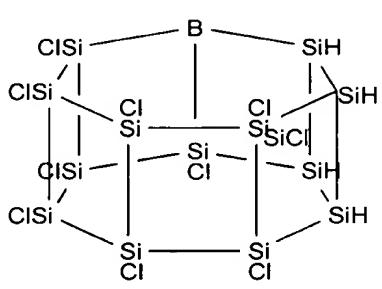
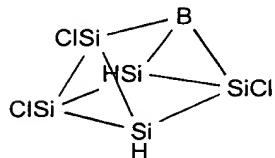
Compound 18



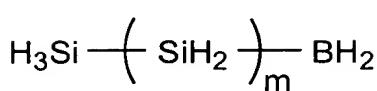
Compound 19



Compound 20

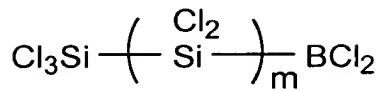


Compound 24



Compound 26

Compound 25



Compound 27

5 Herein, n in Compounds 8, 9, 10, 18, 19, and 20 represents an integer of 0 or more, and n in Compounds 26 and 27 represents an integer of 2 or more. In these formulae, boron-modified silane compounds are shown. Phosphorus-modified silane compounds also have similar backbones to those of the boron-modified silane compounds.

10 In the present invention, the above modified silane compounds may be used alone as a solution, or may be used as a mixture together with the above unmodified silane compounds. The ratio of the modified silane compound to the unmodified silane compound depends on the boron or phosphorus content as a modifying element, and the modifying element is 1 ppb to 25% to silicon atoms.

15 In the present invention, a solution in which the above silicon compound dissolved in a solvent, is applied to an ink jet process. The vapor pressure of the solvent used in the present invention is preferably in a range of 0.001 to 50 mmHg. A vapor pressure exceeding 50 mmHg readily causes nozzle clogging due to drying of droplets discharged by the ink jet process, and will preclude stable discharge. A vapor pressure of less than 0.001 mmHg causes delayed drying of discharged ink. Since the solvent tends to remain in the silicon compound, a high quality silicon film is barely obtained after the heat and/or light treatment in the subsequent step.

20 Solvents used in the present invention, may be, any solvent capable of dissolving the silicon compounds and are unreactive with the silicon compounds.

25 Examples of the solvents include hydrocarbon solvents, such as: n-heptane, n-octane, decane, toluene, xylene, cymene, durene, indene, dipentene, tetrahydronaphthalene, decahydronaphthalene, and cyclohexylbenzene; ether solvents, such as: ethylene glycol dimethyl ether, ethylene glycol diethyl ether, ethylene glycol methyl ethyl ether, diethylene glycol dimethyl ether, diethylene glycol diethyl ether, diethylene glycol methyl ethyl ether, 1,2-dimethoxyethane, bis(2-methoxyethyl)ether, and p-

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dioxane; and polar solvents, such as propylene carbonate, γ -butyrolactone, N-methyl-2-pyrrolidone, dimethylformamide, dimethyl sulfoxide, and cyclohexanone. Among these, hydrocarbon solvents and ether solvents are preferable in view of solubility of silicon compounds and stability thereof. The hydrocarbon solvents are more 5 preferable. These solvents may be used alone or in combinations of two or more. In particular, the hydrocarbon solvents are advantageous, since these exhibit high solubility of the silicon compounds and suppress the remaining silicon compound after the heat treatment and the light treatment, described below.

In the present invention, the ink composition (solution) applied to the ink jet 10 process is prepared by mixing the above silicon compounds and/or the modified silicon compounds as solutes with the above solvents. The concentration of the solutes are determined depending on the required thickness of the silicon film. Preferably, the concentration is 0.01 to 10 percent by weight. When the concentration is less than 0.01%, a uniform coating film is not obtained and discharge operations 15 must be increased. When the concentration exceeds 10%, the viscosity increases and affects discharge.

These solvents may contain a surface tension modifier, such as a fluorine type, a silicon type, or a nonionic type, in a trace amount, if necessary, within a range which 20 does not impair required functions. These solvents may contain a surface tension modifier, such as a fluorine type, a silicon type, or a nonionic type, in a trace amount, if necessary, within a range which does not impair required functions. The nonionic surface tension modifier improves wettability to a workpiece for applying the solution and leveling of the coating film, and prevents graininess and other surface imperfections, for example, an orange peel surface, of the coating film.

25 Examples of such nonionic surfactants include fluorinated surfactants having fluoroalkyl groups or perfluoroalkyl groups, and polyether alkyl surfactants having oxyalkyl groups. Examples of fluorinated surfactants include: $C_9F_{19}CONHC_{12}H_{25}$, $C_8F_{17}SO_2NH-(C_2H_4O)_6H$, $C_9F_{17}O-(PLURONIC\ L-35)-C_9F_{17}$, $C_9F_{17}O-(PLURONIC\ P-84)-C_9F_{17}$, and $C_9F_7O-(TETRONIC-704)-(C_9F_{17})_2$, wherein

PLURONIC L-35 is a polyoxypropylene-polyoxyethylene block copolymer having an average molecular weight of 1,900 made by Asahi Denka Kogyo K.K., PLURONIC P-84 is a polyoxypropylene-polyoxyethylene block copolymer having an average molecular weight of 4,200 made by Asahi Denka Kogyo K.K., and TETRONIC-704 5 is an N,N,N',N'-tetrakis(polyoxypropylene-polyoxyethylene) block copolymer having an average molecular weight of 5,000 made by Asahi Denka Kogyo K.K.

Actual examples of the fluorinated surfactants include Effstop EF301, Effstop EF303, and Effstop EF352 made by Shin Akita Kasei K.K.; Megafack F171 and Megafac F173 made by Dainippon Ink and Chemicals; Asahi Guard AG710 made by 10 Asahi Glass Co., Ltd.; Fluorad FC-170C, Fluorad FC430, and Fluorad FC431 made by Sumitomo 3M Limited; Surflon S-382, Surflon SC101, Surflon SC102, Surflon SC103, Surflon SC104, Surflon SC105, and Surflon SC106 made by Asahi Glass Co., Ltd.; BM-1000 and BM-1100 made by B. M-Chemie; and Schsego-Fluor made by Schwegmann.

15 Polyether alkyl surfactants are polyoxyethylene alkyl ethers, polyoxyethylene allyl ether, polyoxyethylene alkylphenol ethers, polyoxyethylene fatty acid esters, sorbitan fatty acid esters, polyoxyethylene sorbitan fatty acid ethers, and oxyethylene-oxypropylene block copolymers.

Actual examples of these polyether alkyl surfactants include Emulgen 105, 20 Emulgen 430, Emulgen 810, Emulgen 920, Rheodol SP-40S, Rheodol TW-L120, Emanol 3199, Emanol 4110, Excel P-40S, Bridge 30, Bridge 52, Bridge 72, Bridge 92, Arlacel 20, Emasol 320, Tween 20, Tween 60, and Merge 45 made by Kao Corporation; and Nonipol 55 made by Sanyo Chemical Industries, Ltd. Examples of other nonionic surfactants include: polyoxyethylene fatty acid esters, 25 polyoxyethylene sorbitan fatty acid esters, and polyalkylene oxide block copolymers.

Actual Examples of these surfactants are Chemistat 2500 made by Sanyo Chemical Industries, Ltd., SN-EX9228 made by San Nopco Limited, and Nonal 530 made by Toho Chemical Industry Co., Ltd.

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It is preferable that the viscosity of the prepared silicon-compound-containing solution be within a range of 1 to 50 mPa·s. When the viscosity is lower than 1 mPa·s, the peripheral section of the nozzle in the ink jet process is readily contaminated due to overflow of the ink. When the viscosity is higher than 50 mPa·s, the frequency of nozzle clogging increases to preclude smooth discharge of droplets.

Preferably, the surface tension of the silicon-compound-containing solution is in a range of 20 to 70 dyn/cm. A surface tension of less than 20 dyn/cm causes increased wettability of the ink composition to the nozzle surface, resulting in nonlinear flight. A surface tension exceeding 70 dyn/cm causes an unstable meniscus shape at the nozzle tip, resulting in uncontrollability of the discharged volume and discharging timing of the ink composition.

The droplet discharge apparatus in the ink jet process used for supplying the solution in the present invention may be of any mechanism which can discharge appropriate droplets in constant volumes. The apparatus may be of an ink jet process using a piezoelectric element which can form droplets, each weighting approximately several tens nanograms, or of a bubble jet process which forms bubbles by thermal energy from a heater. Moreover, a general coating process, such as: spin coating, dip coating, spray coating, roll coating, or curtain coating, may be combined, if necessary. When the ink composition containing the silicon precursor is applied by the ink jet process, the atmosphere is generally an inert gas, such as argon, helium, or nitrogen, and the temperature is appropriately selected in a range of room temperature to approximately 100°C depending on the ink characteristics.

In the present invention, the substrate used in discharge of the silicon-compound-containing solution by the ink jet process is not limited. Examples of the substrates include general quartz, borosilicate glass, soda glass, transparent electrodes such as: ITO, metallic substrates, e.g., gold, silver, copper, nickel, titanium, aluminum, and tungsten, and glass or plastic substrates coated with these metals.

The coating film of the silicon-compound-containing solution formed by the ink jet process is subjected to a heat and/or light treatment. The treatment is

performed in an inert gas atmosphere, such as nitrogen, argon, and helium. A small amount of reducing gas such as hydrogen may be added, if necessary. The heat treatment is performed for the removal of the solvent and the conversion into a metallic silicon film, after the coating of the ink (solution). The drying treatment, 5 may be, appropriately determined by the boiling point (vapor pressure) and the pressure of the solvent and thermal behavior of the silicon compound, without particular limitation. The conversion into the metallic silicon film is generally performed in an argon atmosphere at, approximately, 100 to 800°C, preferably approximately, 200 to 600°C, and more preferably 300°C to 500°C. In general, an 10 amorphous silicon film is obtained at a final temperature of 550°C or less, whereas a polycrystalline silicon film is obtained at a higher temperature. At a final temperature of less than 300°C, pyrolysis of the silicon compound does not sufficiently proceed, and a silicon film having a sufficient thickness cannot be formed in some cases. The polycrystalline silicon film may also be prepared by conversion of the above 15 amorphous silicon film into the polycrystalline silicon by laser irradiation. The atmosphere in the laser irradiation is preferably an inert gas, such as helium and argon, and may contain a reducing gas, such as hydrogen.

The coating film of the silicon compound formed by the ink jet process in the present invention, may be, subjected to a light treatment in an inert gas atmosphere 20 before, and/or after, removing the solvent in the coating film. The silicon compound soluble in solvents is converted into a tough coating film, which is insoluble in the solvents, by the ring cleavage reaction, by means of this light treatment. Moreover, the heat treatment, which is performed after the light treatment or simultaneously 25 performed with the light treatment, converts the silicon film into one having superior optical and electrical characteristics.

Examples of light sources used in the present invention include: low-pressure or high-pressure mercury lamps, deuterium lamps, discharge light of rare gases, such as argon, krypton, and xenon, YAG lasers, argon lasers, carbon dioxide lasers, excimer lasers of XeF, XeCl, XeBr, KrF, KrCl, ArF, and ArCl. These light sources

DO NOT DESTROY

generally have power in a range of 10 to 5,000 W, and a power of 100 to 1,000 W is adequate in the present invention. The wavelengths of these light sources are not limited, as long as the light is absorbed in the coating film of the photo-ring-cleavage silicon compound to some extents, and are generally in a range of 170 nm to 600 nm.

5 The use of laser light is, particularly preferable, in view of conversion efficiency into the polycrystalline silicon film. The temperature for the light treatment is generally in a range of room temperature to 500°C, and can be appropriately determined depending on the semiconductive characteristics of the resulting silicon film.

The present invention will now be described in more detail with reference to the Examples, but should not be limited to these Examples.

In these Examples, the viscosity and the surface tension of each ink composition indicate values at 20°C.

(EXAMPLE 1)

A silicon-compound-containing solution (ink) is prepared by dissolving 0.05 g of cyclopentasilane into a mixed solvent of 7 g of decahydronaphthalene and 3 g of tetrahydronaphthalene. The viscosity of the solution is 3.2 mPa·s and the surface tension is 33 dyn/cm. Fig. 1 shows the patterning of silicon thin films by an ink jet process in accordance with this example. The silicon-compound-containing ink 11 is pattern-coated onto a quartz substrate 13 using an ink jet head 12 composed of a piezoelectric element in an argon atmosphere. The substrate is dried at 200°C, in an argon atmosphere, and is pyrolyzed, at 500°C, to form a pattern of metallic silicon films 15 (film regions, each having a diameter of 50 μm), each having a thickness of 35 nm, shown in Figs. 1(b) and 1(c). Fig. 1(b) is a cross-sectional view of the top view of Fig. 1(c). A surface analysis of the silicon film by ESCA detects only silicon atoms. The crystal state of the silicon film by a Raman spectrum is 100% amorphous. The amorphous silicon films are irradiated with an excimer laser having a wavelength of 308 nm and an energy density of 300 mJ/cm² in an argon atmosphere to form a pattern of polycrystalline silicon films 16 (film regions, each having a diameter of 50 μm) shown in Fig. 1(d). The Raman spectrum shows that the crystallinity is 80%.

(EXAMPLE 2)

A silicon-compound-containing solution (ink) is prepared by dissolving 0.2 g of hexachlorocyclohexasilane into a mixed solvent of 5 g of cyclohexylbenzene and 5 g of cymene. The viscosity of the solution was 4.8 mPa·s and the surface tension is 32 dyn/cm. Fig. 2 shows the patterning of silicon thin films by an ink jet process in accordance with this example. The silicon-compound-containing ink 21 is pattern-coated onto a quartz substrate 23 using an ink jet head 22 composed of a piezoelectric element in an argon atmosphere. The substrate is dried at 250°C in an argon atmosphere containing 5% hydrogen and is heat-treated at 450°C while being irradiated with ultraviolet light from a 500-W high-pressure mercury lamp for 30 minutes to form a pattern of metallic silicon films 25 (film regions, each being 50 × 50 μm), each having a thickness of 80 nm, shown in Figs. 2(b) and 2(c). A surface analysis of the silicon film, by ESCA, detects only silicon atoms. The crystal state of the silicon film, by a Raman spectrum, is 100% amorphous. The amorphous silicon film was heat-treated at 800°C, in an argon/hydrogen atmosphere, to form a pattern of a polycrystalline silicon film 26 (film region of 50 × 50 μm) having a crystallinity of 50%, shown in Fig. 2(d).

(EXAMPLE 3)

A silicon-compound-containing solution (ink) is prepared by dissolving 0.1 g
20 of 1-borahexaprismane (Compound 11) into a mixed solvent of 7 g of
tetrahydronaphthalene and 3 g of cyclohexylbenzene. The viscosity of the solution is
4.2 mPa·s and the surface tension is 36 dyn/cm. Fig. 3 shows the patterning of silicon
thin films by an ink jet process in accordance with this example. The silicon-
compound-containing ink 31 is pattern-coated onto a quartz substrate 33 using an ink
25 jet head 32 composed of a piezoelectric element in an argon atmosphere. The
substrate is dried at 250°C in an argon atmosphere and was pyrolyzed at 500°C to
form a pattern of metallic silicon films 35 (film regions, each having a diameter of 50
μm), each having a thickness of 70 nm, shown in Figs. 3(b) and 3(c). A surface
analysis of the silicon film, by ESCA, detects only silicon atoms and boron atoms and

the ratio thereof is 5:1. The crystal state of the silicon film, by a Raman spectrum, is 100% amorphous. The amorphous silicon films are irradiated with an excimer laser having a wavelength of 308 nm and an energy density of 350 mJ/cm² in an argon atmosphere to form a pattern of polycrystalline silicon films 36 (film regions, each 5 having a diameter of 50 μm) shown in Fig. 3(d). The Raman spectrum shows that the crystallinity was 75%.

(EXAMPLE 4)

A silicon-compound-containing solution (ink) is prepared by dissolving 0.05 g of 1-phosphocyclopentasilane into a mixed solvent of 8 g of decahydronaphthalene 10 and 2 g of cyclohexylbenzene. The viscosity of the solution is 4.0 mPa·s and the surface tension is 36 dyn/cm.

Fig. 4 shows the patterning of silicon thin films by an ink jet process in accordance with this example. The silicon-compound-containing ink 41 is pattern-coated onto a quartz substrate 43 using an ink jet head 42 composed of a piezoelectric 15 element in an argon atmosphere. The substrate is dried at 150°C in an argon atmosphere containing 5% hydrogen while being irradiated with ultraviolet light from a 500-W high-pressure mercury lamp for 10 minutes to form a tough coating film of polysilazane which is insoluble in solvents by a ring cleavage reaction. The coating film is pyrolyzed at 500°C in an argon atmosphere to form a pattern of metallic silicon 20 films 45 (film regions, each being 50 \times 50 μm), each having a thickness of 25 nm, shown in Figs. 4(b) and 4(c). A surface analysis of the silicon film, by ESCA, detects only silicon atoms and phosphorus atoms and the ratio thereof is 5:1. The crystal state of the silicon film, by a Raman spectrum, is 100% amorphous. The amorphous silicon films are irradiated with an excimer laser having a wavelength of 308 nm and 25 an energy density of 300 mJ/cm² in an argon atmosphere to form a pattern of polycrystalline silicon films 46 (film regions, each being 50 \times 50 μm) shown in Fig. 4(d). The Raman spectrum shows that the crystallinity was 75%.

(EXAMPLE 5)

A silicon-compound-containing solution (ink) is prepared by dissolving 0.5 g of silylcyclopentasilane into a mixed solvent of 5 g of decahydronaphthalene and 5 g of tetrahydronaphthalene. The viscosity of the solution is 5.2 mPa·s and the surface tension is 34 dyn/cm. Fig. 5 shows the patterning of silicon thin films by an ink jet process in accordance with this example. The silicon-compound-containing ink 51 is pattern-coated onto a polyimide film substrate 53 using an ink jet head 52 composed of a piezoelectric element in an argon atmosphere. The substrate is dried at 200°C in an argon atmosphere and is irradiated using a 500-W high-pressure mercury lamp at 350°C for photolysis and pyrolysis to form a pattern of metallic silicon films 55 (film regions, each having a diameter of 70 µm), each having a thickness of 80 nm, shown in Fig. 5(b). A surface analysis of the silicon film by ESCA detects only silicon atoms. The crystal state of the silicon film, by a Raman spectrum, is 100% amorphous.

(EXAMPLE 6)

A (p-type) silicon-compound-containing solution (ink) is prepared by dissolving 0.01 g of 1-boracyclopentasilane and 0.1 g of cyclopentasilane into a mixed solvent of 5 g of tetrahydronaphthalene and 5 g of cyclohexylbenzene. The viscosity of the solution is 3.8 mPa·s and the surface tension is 35 dyn/cm. Next, a (n-type) silicon-compound-containing solution (ink) is prepared by dissolving 0.01 g of 1-phosphocyclopentasilane and 0.1 g of cyclopentasilane into a mixed solvent of 5 g of tetrahydronaphthalene and 5 g of cyclohexylbenzene. The viscosity of the solution is 3.7 mPa·s and the surface tension is 36 dyn/cm. Fig. 6 shows the patterning of n-type and p-type silicon thin films by an ink jet process in accordance with this example.

The (n-type) silicon-compound-containing ink 61 and the (p-type) silicon-compound-containing ink 64 are pattern-coated onto a quartz substrate 63 using an ink jet head 62 composed of a piezoelectric element in an argon atmosphere. The substrate is dried at 250°C, in an argon atmosphere containing 5% hydrogen, and is pyrolyzed at 500°C to form a pattern including n-type silicon films 65 (film regions, each being 25 µm in diameter and 60 nm in thickness).

50 × 50 μm) and p-type silicon films^{25p} (film regions, each being 50 × 50 μm) shown in Figs. 6(b) and 6(c). According to a surface analysis of the silicon films by ESCA, the ratio of silicon atoms and phosphorus atoms is 50:1 in the n type and the ratio of silicon atoms and phosphorus atoms is 50:1 in the p type. The crystal state of the silicon films, by a Raman spectrum, is 100% amorphous. The amorphous silicon films are irradiated with an excimer laser having a wavelength of 308 nm and an energy density of 320 mJ/cm² in an argon atmosphere to form a pattern of n-type and p-type polycrystalline silicon films^{66n and 66p}, respectively, (film regions, each being 50 × 50 μm) shown in Fig. 6(d). The Raman spectrum shows that the crystallinity is 75%.

10 (EXAMPLE 7)

A silicon-compound-containing solution (ink) is prepared by dissolving 0.05 g of octasilacubane (Compound 2) into a mixed solvent of 5 g of decahydronaphthalene and 5 g of tetrahydronaphthalene. The viscosity of the solution is 5.5 mPa·s and the surface tension is 34 dyn/cm. Fig. 7 shows the patterning of silicon thin films by an ink jet process in accordance with this example. The silicon-compound-containing ink 71 is pattern-coated onto a quartz substrate 73 using an ink jet head 72 composed of a piezoelectric element in an argon atmosphere containing 3% hydrogen. The substrate is irradiated with using a high-pressure mercury lamp of 500 W at room temperature for 5 minutes in an argon atmosphere containing 3% hydrogen. As a result, polyhydrosilane films, which are insoluble in solvents, were formed. The films are pyrolyzed in the argon atmosphere containing 3% hydrogen at 500°C to form a pattern of metallic silicon films 75 (film regions, each having a diameter of 50 μm), each having a thickness of 35 nm, shown in Figs. 7(b) and 7(c). Fig. 7(b) is a cross-sectional view and Fig. 7(c) is a top view corresponding to Fig. 7(b). A surface analysis of the silicon film, by ESCA, detects only silicon atoms. The crystal state of the silicon film, by a Raman spectrum, is 100% amorphous. The amorphous silicon films are irradiated with an excimer laser having a wavelength of 308 nm and an energy density of 300 mJ/cm² in an argon atmosphere to form a pattern of

polycrystalline silicon films 76 (film regions, each having a diameter of 50 μm) shown in Fig. 7(d). The Raman spectrum shows that the crystallinity is 80%.

(Example 8)

The silicon-compound-containing solution of Example 7 is prepared and
5 pattern-coated onto a quartz substrate using an ink jet head composed of a piezoelectric element in an argon atmosphere containing 3% hydrogen. The substrate is dried at 150°C in an argon atmosphere containing 3% hydrogen, and simultaneously is irradiated using a 500 W high-pressure mercury lamp for 5 minutes. As a result, polyhydrosilane films, which are insoluble in solvents, are formed. The
10 films are pyrolyzed, as in Example 7, to form a pattern of amorphous metallic silicon films, as in Example 7. The amorphous silicon films are irradiated with an excimer laser having the wavelength and the same energy density as in Example 7, in air, to form a pattern of polycrystalline silicon films 76 (film regions, each having a diameter of 50 μm) shown in Fig. 7(d). The Raman spectrum shows that the crystallinity was
15 60%.

According to the present invention, as described above, a composition containing a silicon precursor is pattern-coated by an ink jet process, and a desired silicon film (pattern) as an electronic material, can be formed by a novel liquid phase process, which is different from conventional methods for forming silicon film, by
20 means of thermal and/or optical energy.

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INDUSTRIAL APPLICABILITY

Since the present invention prevents the generation of powder during the formation of the silicon film and does not use a large vacuum process, unlike
25 conventional CVD processes, the present invention does not require expensive equipment and can form a film on a substrate having a large area using minimum amounts of materials. Since the silicon film pattern can be formed without a photolithographic etching process, semiconductor devices having silicon films, such

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as LSIs, thin-film transistors, photoelectric transducers, and photosensitive members, the film patterning process reduces costs and energy consumption.